PHYSICAL REVIEW B VOLUME 49, NUMBER 7 15 FEBRUARY 1994-I

Energy loss in fast-particle surface scattering at grazing incidence

J. R. Manson
Department of Physics and Astronomy, Clemson University, Clemson, South Carolina 29634

R. H. Ritchie
Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
and Department of Physics, University of Tennessee, Knoxville, Tennessee 37996
(Received 8 September 1993)

The surface scattering of kilovolt-energy ions and atoms at glancing-incidence angles has contributed substantially to knowledge of elementary electronic excitations in the interface region. We consider the influence of inelastic exchange of mechanical energy, due to recoil of the target atoms, on the distribution of scattered projectile atoms. Although with a glancing-incident-angle geometry the relative energy loss by this mechanism is small, it can have a substantial effect on the angular distribution of the scattered particles. These conclusions are supported by numerical calculations of energy losses and scattered particle distributions.

I. INTRODUCTION

The scattering of hyperthermal ions and atoms from solids, in the range of incident energies from a few hundreds of eV to a few tens of keV, can excite a large range of fundamental excitations in solids. When directed at a target at sufficiently grazing angles, a large fraction of these high-energy projectiles do not penetrate the surface but are reflected back into the space above the target. In this case the information carried by the reflected particles is extremely surface sensitive, and the method is used as a probe of surface properties.[1–3]

Recently, in a series of careful experiments, Winter and co-workers have demonstrated the effectiveness of fast-ion and fast-neutral-atom collisions at grazing incidence on surfaces as a method for exploring the nature of the attractive charge-surface potential.[4–7] In these experiments a monoenergetic and well-collimated beam of ions with energies in the kilovolt range is directed toward a clean and atomically flat metal surface at a grazing angle of about one degree. The grazing-incidence configuration means that the velocity normal to the surface is small compared to the total translational velocity. Owing to the low energy associated with the normal velocity, the particles are repelled by the repulsive potentials of the outermost layer of surface atoms, and for a defect-free surface virtually all the incident ions are reflected backward and penetration of the ions into the solid is negligible.

At these energies the dominant mechanisms for energy loss are electronic, including excitation of elementary and collective electronic excitations in the solid and charge-transfer processes. As an ion approaches the surface from afar, it first experiences the polarization or image potential which accelerates it toward the surface, but the image potential is always small compared to the total translational energy. For neutral atoms, the polarization potential is the Van der Waals potential which is in the millivolt range and is totally negligible at these energies. Near the surface the number of possible different types of electronic interactions becomes large and can even include entering quasibound states in the attractive well. However, one mechanism of interest is the charge exchange, and in the case of incident ions its is found that a significant and readily measurable fraction of the incident ions leave the surface as neutrals. By observing the differences in the scattered distribution of neutrals and ions, it is possible to estimate the strength of the image potential at the point of charge transfer and neutralization. The signature of this effect is quite striking; the peak in the scattered distribution of neutrals is distinctly shifted with respect to that of the ions. An even greater effect is observed when the scattered distribution of incident neutrals is compared with that of incident ions of the same species. The peak of the outgoing neutrals is observed to be separated from that of the ions by more than one degree in the case of 25-keV Ar and 25-keV Ar^{6+}.[4–6]

In the analysis of these experiments the energy losses of the incident projectiles due to excitation of the vibrational modes of the target have been neglected. Excitation of the vibrational modes, which at these high probe energies is perhaps more correctly termed direct mechanical energy loss, is expected to be quite small compared to the electronic losses. The purpose of this work is to investigate the size and nature of these mechanical energy losses and to determine the effect they have on the shape of the distribution of scattered particles. In order to separate clearly the purely mechanical effects from the electronic mechanisms, we treat the incident projectiles as neutral particles.

In spite of the very high energy of the projectiles compared to typical vibrational-energy quanta, the low energy associated with the normal motion and the back-scattering nature of the process allow us to utilize theoretical methods developed for the classical limit of the scattering of neutral atoms from surfaces, and this theory is briefly developed in the next section. Several

0163-1829/94/49(7)/4881(5)/$06.00

calculations of angular distributions and energy losses of the scattered lobes are presented in Sec. III, and we find the mechanical losses can have a strong effect on the scattering. A few concluding remarks are made in Sec. IV.

II. THEORETICAL BACKGROUND

An appropriate theoretical framework for describing the experiments of Winter and co-workers[4–6] can be developed using methods for handling molecule-surface collisions at high temperatures and high energies.[8–17] Although the energies involved would suggest that a classical theory would suffice, we begin with purely quantum-mechanical expressions and then go to the limit of large energy exchanges via the correspondence principle. The transition rate $w(\mathbf{k}_f,\mathbf{k}_i)$ for a particle making a transition from the initial incident beam of momentum $\hbar\mathbf{k}_i$ to a final state denoted by momentum $\hbar\mathbf{k}_f$ is

$$w(\mathbf{k}_f,\mathbf{k}_i)=\frac{2\pi}{\hbar}\left\langle\!\!\left\langle \sum_{\{n_f\}} |T_{fi}|^2\delta(E_f-E_i)\right\rangle\!\!\right\rangle . \tag{1}$$

This is the generalized Fermi golden rule, averaged over initial states of the target as denoted by $\langle\langle\cdots\rangle\rangle$, and summed over final states $\{n_f\}$ of the target. All measurable quantities in a scattering experiment are proportional to the transition rate. For example, the three-dimensional differential reflection coefficient is obtained by dividing $w(\mathbf{k}_f,\mathbf{k}_i)$ by the incident flux and multiplying by the appropriate density of states in final momentum space,

$$\frac{d^3R}{d\Omega_f dE_f}=\frac{L^4}{(2\pi\hbar)^4}\frac{m^2|\mathbf{k}_f|}{k_{iz}}w(\mathbf{k}_f,\mathbf{k}_i) , \tag{2}$$

where L is the quantization length parallel to the surface, k_{iz} is the normal component of the incident wave vector, and m is the projectile mass.

For fast incident particles, the scattering time is short compared to a phonon vibrational period or a recoil time of a surface atom. Hence we can use the quick-collision approximation. This approximation is equivalent to stating that the displacement of a target atom $\mathbf{u}_l$ enters only in the overall phase of the transition matrix. We write the transition operator as a sum of contributions from all unit cells of the target,

$$T=\sum_l T^l . \tag{3}$$

When taking matrix elements of the transition operator, it is natural to separate explicitly the phase factor which accounts for differences in optical paths for scattering from different parts of the surface.

$$T_{\mathbf{k}_f,\mathbf{k}_i}=(\mathbf{k}_f|T|\mathbf{k}_i)=\sum_l e^{-i\mathbf{k}\cdot[\mathbf{r}_l+\mathbf{u}_l(t)]}\tau_{\mathbf{k}_f,\mathbf{k}_i} , \tag{4}$$

where $\mathbf{r}_l$ is the equilibrium position of the lth target center, $\tau_{\mathbf{k}_f,\mathbf{k}_i}$ is the scattering amplitude of a surface unit cell, and $\mathbf{k}=\mathbf{k}_f-\mathbf{k}_i$. The quick-collision approximation is equivalent to assuming that the scattering amplitude is independent of lattice displacement $\mathbf{u}_l$, and the only dependence on displacement is in the phase factor.

When the transition matrix (4) is inserted in the transition rate (1), and the limit of high temperature and high energy is taken, the result is a simple closed-form expression for the differential cross section of back-reflected particles:

$$\frac{d^3R}{d\Omega_f dE}=\frac{m^2|\mathbf{k}_f|}{4\pi^3\hbar^5 k_{iz}S_{\mathrm{UC}}}|\tau_{\mathbf{k}_f,\mathbf{k}_i}|^2 v_R^2\left\{\frac{\hbar^2\pi}{\Delta E_0 k_B T}\right\}^{3/2} \times\exp\left\{-\frac{(\Delta E+\Delta E_0)^2+2\hbar^2 v_R^2 K^2}{4k_B T\Delta E_0}\right\} , \tag{5}$$

where $\mathbf{K}$ is the component of $\mathbf{k}$ parallel to the surface, T is the surface temperature, and S_{UC} is the area of a surface unit cell. Specifically, the condition for the validity of this expression is that the Debye-Waller factor should be very small. The Debye-Waller factor is given by $\exp(-2W)$ with $W=\langle\langle(\mathbf{k}\cdot\mathbf{u}_l)^2\rangle\rangle/2$, and the necessary condition can be expressed as $2W\gg 1$ which is well satisfied for the present experiments of interest.

Equation (5) has the form of a Gaussian in energy exchange ΔE, with the origin shifted by $-\Delta E_0$, and multiplied by a Gaussian in the parallel momentum transfer $\hbar\mathbf{K}$. Actually, it is not a true Gaussian; rather it is a very strongly skewed function of ΔE due to the energy dependence of ΔE_0, which is given explicitly by

$$\Delta E_0=\frac{\hbar^2 k^2}{2M} , \tag{6}$$

where M is the mass of a target atom. On physical grounds it is easy to see that the scattered energy distribution cannot be a symmetric function of ΔE. At low energies, $\mathbf{k}_f\to 0$, the cross section must vanish because an incident particle can lose at most an amount of energy equal to its incident energy. However, on the energy-gain side there is no upper limit to the amount of energy that it is possible for a scattered particle to gain (although such large-energy-gain events are highly improbable).

The Gaussian function of parallel momentum transfer appearing in (5) is a structure-factor effect due to vibrational correlations between the target atoms, and takes into account the fact that the incident projectile interacts with a large number of surface particles. Its strength depends on the size of v_R, which is a weighted average sound velocity parallel to the surface.[12]

The multiplicative factor $(k_B T\Delta E_0)^{-3/2}$ assures that, as the width of the skewed Gaussian grows with increasing $|E_i|$ and T (the width increases roughly as $\sqrt{k_B T\Delta E_0}$ in energy units), the height of the distribution decreases in the correct proportion in order to conserve the total number of scattered particles. The factor $|\tau_{\mathbf{k}_f,\mathbf{k}_i}|^2$ in (5) is the form factor for scattering by a unit cell of the surface. For the present purposes we take it to be the form factor for scattering by a rigid wall in the semiclassical limit,

$$|\tau_{\mathbf{k}_f,\mathbf{k}_i}|=2\hbar^2 k_f\cos(\theta_f)k_i\cos(\theta_i)/m , \tag{7}$$

where the initial and final angles, θ_i and θ_f, are measured with respect to the surface normal. In this case the specific form of $|\tau_{\mathbf{k}_f,\mathbf{k}_i}|$ plays little role in the results because it is a relatively slowly varying function of the momenta.

Equation (5) gives the differential reflection coefficient as a function of final solid angle and energy. Often only the angular distribution is measured, and this is given by

$$\frac{d^2R}{d\Omega_f}=\int dE_f \frac{d^3R}{d\Omega_f dE_f} \ . \tag{8}$$

Also an important measurable quantity is the average energy loss, given by

$$\overline{\Delta E}=\int dE_f d\Omega_f \Delta E \frac{d^3R}{d\Omega_f dE_f} \ . \tag{9}$$

It is of interest to compare $\overline{\Delta E}$ to ΔE_0, in the light of the semiclassical trajectory approximation. This approximation assumes that the projectile follows the classical trajectory of an elastic and specularly scattered particle, and the energy losses are treated as a small, higher-order correction. This is the limiting case in which ΔE_0, as well as $|\tau_{\mathbf{k}_f,\mathbf{k}_i}|$, is approximately constant and for which it is readily shown that $\overline{\Delta E}=\Delta E_0$. Thus the deviation of $\overline{\Delta E}$ from ΔE_0 is an indication of the validity of the semiclassical trajectory approximation.

In treating high-energy projectile-surface interactions one can invoke a hard-cubes approximation which essentially states that parallel momentum is conserved in the scattering process, i.e., $\mathbf{K}=0$, which is the same as

$$k_f \sin(\theta_f)=k_i \sin(\theta_i) \ . \tag{10}$$

This introduces a δ function under the integral on the right-hand side of Eq. (8), and leads to a differential reflection coefficient $d^2R/d\Omega_f$, which is equivalent to the form obtained from Eq. (5) in the limit $v_R \to \infty$.

A very simple approximate relation for the angular position of the final scattered beam is obtained by combining the momentum conservation relation of (10) with the semiclassical energy loss, expressed as

$$E_f=E_i-\Delta E_0 \ . \tag{11}$$

The result depends only on the projectile-to-surface-atom mass ratio m/M and is

$$\sin(\theta_f-\theta_i)=\frac{m}{M}\sin(\theta_f+\theta_i) \ . \tag{12}$$

For $m/M<1$ and grazing incidence, this is well approximated by

$$\theta_f-\theta_i=\frac{(2m/M)(\frac{1}{2}\pi-\theta_i)}{1+(m/M)} \ . \tag{13}$$

III. CALCULATIONS

As stated above in Sec. I, we consider in this work only energy losses due to mechanical excitation of the surface. Thus since the major channels of energy loss due to electronic excitations are excluded, we cannot expect to compare directly to experiment. However, we have carried out a number of numerical calculations in order to assess the importance of the purely mechanical losses.

The quantity of interest to calculate which can be compared qualitatively to experiment is the angular distribution, or more precise the reflection coefficient per solid angle $d^2R/d\Omega_f$, and this is compared with the maximum value of the total differential reflection coefficient $\max[d^3R/d\Omega_f dE_f]$. We also examine the relevance of the approximation of parallel momentum conservation $\mathbf{K}=0$ and calculate $d^2R/d\Omega_f$ under this condition. (In general this turns out to be a very poor representation of the exact $d^2R/d\Omega_f$.) Finally, we calculate the average energy loss $\overline{\Delta E}$ and compare this to the semiclassical trajectory value of ΔE_0.

Figure 1 shows $d^2R/d\Omega_f$, $\max[d^3R/d\Omega_f dE_f]$, and $d^2R/d\Omega_f$ calculated under the condition $\mathbf{K}=0$ as a function of final scattered polar angle for the scattering of 25-keV Na off an Al surface at an incident angle of $\theta_i=89°$ (a grazing angle of 1° with respect to the plane of the surface). The value of v_R is 3200 m/s, which corresponds to the velocity of the acoustic Rayleigh mode on an Al(111) surface.[18] All of these curves are strikingly different, and clearly the hard-cubes approximation of conservation of parallel momentum is not at all a good representation of the correct $d^2R/d\Omega_f$. The shape of $d^2R/d\Omega_f$ is rather broad and it is peaked at about 87° which is closer to the normal than the incident beam. By contrast, the approximation $\mathbf{K}=0$ leads to a very narrow outgoing distribution, peaked at an angle of 89.7°, much closer to the surface plane.

Figure 2 shows the exact expression for $d^2R/d\Omega_f$ plotted for several values of v_R. The curve for $v_R=3200$ m/s is the same as in Fig. 1(a), the value of $v_R=5000$ m/s is a representative maximum phonon velocity of bulk Al,[19] and the two curves for $v_R=10^4$ m/s and $v_R=10^5$ m/s show the approach to the form for $\mathbf{K}=0$. The average energy losses range from 199 eV, or a fractional loss

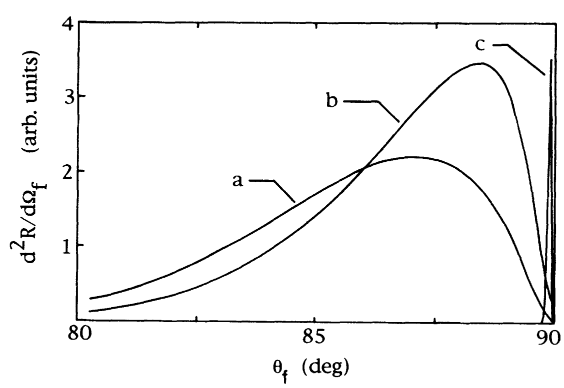

FIG. 1. Scattered intensity distribution for 25-keV Na incident on an Al surface at an angle of 89°. (a) The two-dimensional differential reflection coefficient $d^2R/d\Omega_f$; (b) the maximum value of the three-dimensional differential reflection coefficient, $\max[d^3R/d\Omega_f dE_f]$; (c) the differential reflection coefficient with the condition $\mathbf{K}=0$. The sound velocity v_R is 3200 m/s.

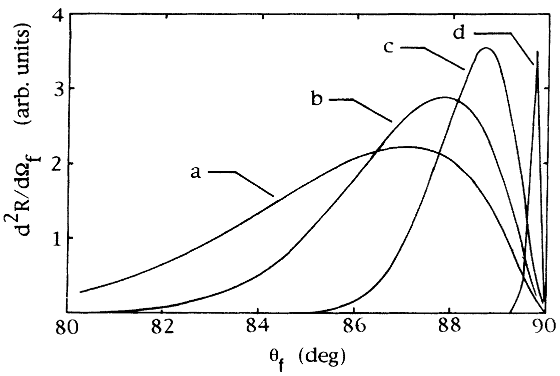

FIG. 2. Two-dimensional differential reflection coefficient for 25-keV Na incident on an Al surface at an angle of 89°. (a) $v_R = 3200$ m/s, same as Fig. 1(a); (b) $v_R = 5000$ m/s; (c) $v_R = 10^4$ m/s; and (d) $v_R = 10^5$ m/s.

of 0.008 for $v_R = 3200$ m/s, to a fractional energy loss of 0.002 for $v_R = 10^4$. These are larger energy losses than the value of $\Delta E_0 = 25.0$ eV given by the semiclassical expression (6).

It is also of interest to consider a case for which the angle of incidence is not quite such a grazing geometry as that of Figs. 1 and 2. In Fig. 3 we consider the same projectile and surface but with an incidence angle of 80°. We find that for $v_R = 3200$ m/s the differential reflection coefficient is peaked at an angle of about $\theta_f = 85°$. The $\max d^3R/d\Omega_f dE_f$ curve in this case is almost identical to $d^2R/d\Omega_f$, while the differential reflection coefficient calculated with $\mathbf{K} = 0$ is very strongly peaked near the surface at about $\theta_f = 89°$. Again we note that the effect of inelastic exchange due to mechanical energy losses is quite noticeable, and causes a large deviation of the scattered lobe from the specular direction towards the surface rather than away from the surface, as was found for the more grazing incidence of Fig. 1.

Figure 4 is similar to Fig. 2, except for the incidence angle of 80°. Again, this shows the approach of $d^2R/d\Omega_f$ to the parallel momentum conservation expression as v_R becomes large. The energy losses range from $\overline{\Delta E} = 1.62$ keV for $v_R = 3200$ m/s to $\overline{\Delta E} = 0.96$ keV

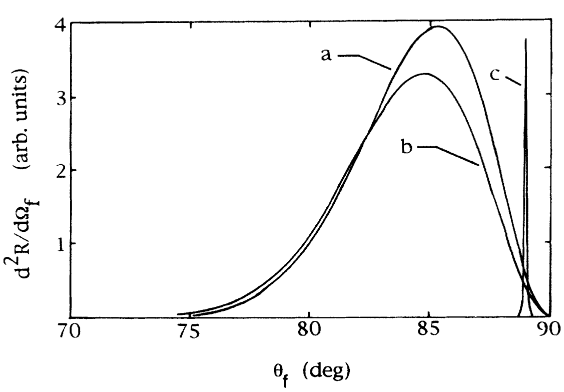

FIG. 3. Same as Fig. 1, except for an incident angle of 80°.

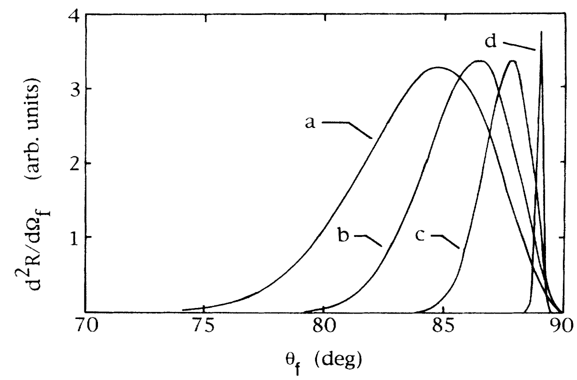

FIG. 4. Same as Fig. 2, except for an incident angle of 80°.

at the large value of $v_R = 10^4$ m/s. In this case the semiclassical energy exchange $\Delta E_0 = 2.48$ keV, considerably larger than the values of $\overline{\Delta E}$.

IV. CONCLUSIONS

We have considered the effect of mechanical energy losses on the scattered distributions of particles when a relatively high-energy beam of atoms or ions is directed toward a surface at grazing incidence. Although this energy ultimately winds up as heat in the vibrational modes, the initial exchange is due to recoil of the surface atoms rather than the creation and annihilation of phonon modes. Totally neglected in this approach is any exchange with elementary or collective electronic excitations, which are the dominant contributors to energy losses in such collisions. The object is to study the effect of purely mechanical losses and to determine if such losses have an appreciable effect.

We find that the scattered lobe can be considerably affected by these processes and can deviate strongly from the specular direction. The energy losses, although only a small fraction of the incident translational energy, can be significant.

We have demonstrated that energy loss processes through purely mechanical exchange can have an important effect on the distribution of the scattered lobe of projectiles. Such effects are sometimes neglected in the interpretation of high-energy ion-surface scattering experiments. This work indicates that such effects are important and should be accounted for in any subtle interpretation of the experimental results.

ACKNOWLEDGMENTS

This research was sponsored jointly by the Office of Health and Environmental Research, U.S. Department of Energy, under Contract No. DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. J.R.M. would like to thank the Alexander von Humboldt foundation for support, and the Service de Recherche sur les Surfaces et l'Irradiation de la Matière of the Centre d'Études de Saclay for hospitality during the course of this work. This work was supported by the NSF under Grant No. DMR 9114015.

[1]H. J. Andrä, in *Fundamental Processes of Atomic Dynamics,* edited by J. S. Briggs (Plenum, New York, 1988).
[2]C. Höfner, A. Närmann, and W. Heiland, Nucl. Instrum. Methods B **72**, 227 (1992).
[3]A. Närmann, H. Franke, K. Schmidt, A. Arnau, and W. Heiland, Nucl. Instrum. Methods B **69**, 158 (1992).
[4]H. Winter, J. Leuker, M. Sommer, and H.W. Ortjohann, in *Proceedings of the 14th Werner Brandt Workshop,* edited by R.H. Ritchie (ORNL, Oak Ridge, 1992), p. 38.
[5]H. Winter, Europhys. Lett. **18**, 207 (1992).
[6]H. Winter, Phys. Rev. A **46**, R13 (1992).
[7]H. Winter and R. Zimny, in *Coherence in Atomic Collisions Physics,* edited by H. J. Beyer *et al.* (Plenum, New York, 1988), p. 283.
[8]W. Brenig, Z. Phys. B **36**, 81 (1979).
[9]A. C. Levi, Nuovo Cimento B **54**, 357 (1979).
[10]A. C. Levi and H. Suhl, Surf. Sci. **88**, 221 (1979).
[11]R. Brako and D. M. Newns, Phys. Rev. Lett. **48**, 1859 (1982).
[12]R. Brako and D. M. Newns, Surf. Sci. **123**, 439 (1982).
[13]David A. Micha, J. Chem. Phys. **74**, 2054 (1981).
[14]J. Böheim and W. Brenig, Z. Phys. B **41**, 243 (1983).
[15]H. D. Meyer and R. D. Levine, Chem. Phys. **85**, 189 (1984).
[16]V. Celli, D. Himes, P. Tran, J. P. Toennies, Ch. Wöll, and G. Zhang, Phys. Rev. Lett. **66**, 3160 (1991).
[17]J. R. Manson, Phys. Rev. B **43**, 6924 (1991).
[18]W. Kress, in *Surface Phonons,* edited by W. Kress and F. W. deWette, Springer Series in Surface Sciences Volume 21 (Springer, Heidelberg, 1991), p. 209.
[19]G. E. Becker, in *Chemical Rubber Handbook,* edited by Robert C. Weast (Chemical Rubber, Cleveland, 1970), p. E-41.